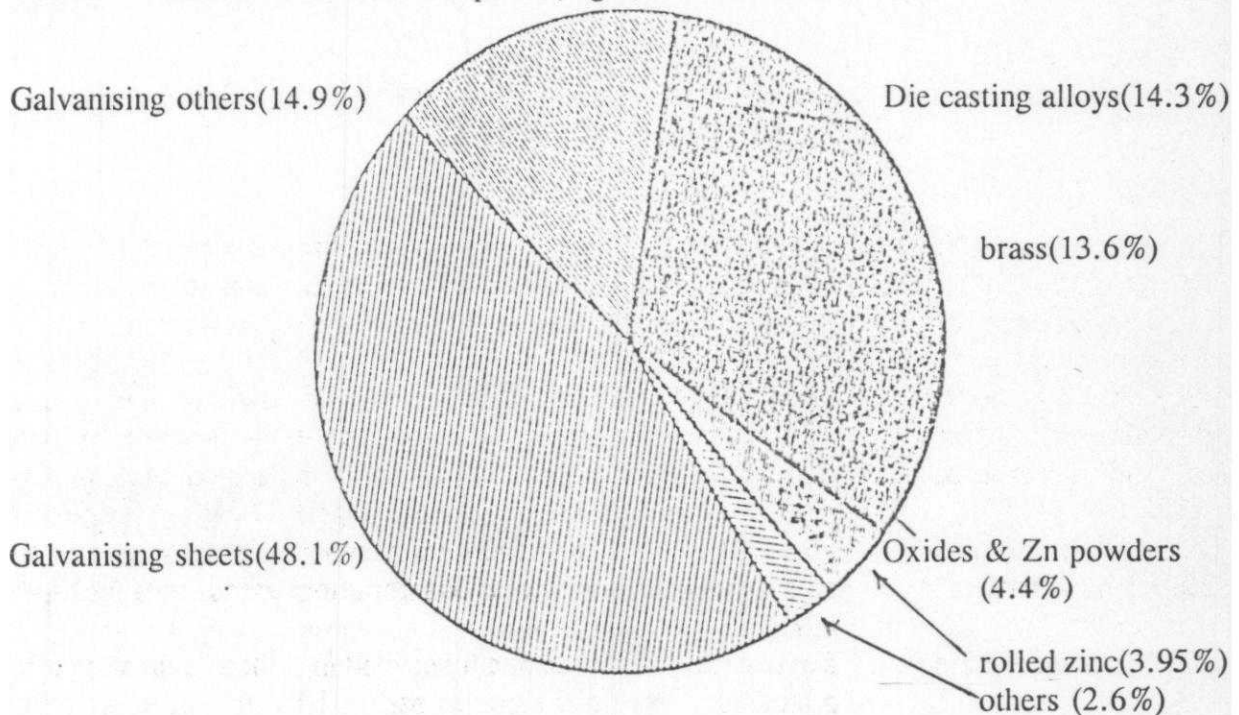


# CORROSION BEHAVIOUR OF GALVANISED PRODUCTS

**Inder Singh**  
**National Metallurgical laboratory**  
**Jamshedpur-831 007**

On tonnage basis atmospheric corrosion of metals and alloys is one of the serious corrosion problems in the modern civilization because of its considerable effect on GNP of the country. The commonest cause of rapid atmospheric corrosion is the presence of acidic gases, such as sulphur dioxides, hydrogen sulphide or hydrogen chloride or of suspended salts like ammonium sulphate or sodium chloride. The acidic gases resulted on with the rapid industrialization, pose enormous corrosion problem if it is unchecked. Generally, the atmospheric corrosion is minimised by (i) eliminating corrosion constituents from the atmosphere, (ii) selecting a material possessing maximal resistance or (iii) by interposing a protective coating in between the metal and the corrosive atmosphere. Methods based on avoiding atmospheric pollution and selecting an atmospheric corrosion resistance metals and alloys have their limitations on practical as well as on economic grounds. So, interposition of a protective coating in between the metal and the corrosive atmosphere is considered most appropriate in view of its case of application and economic benefits.

Almost 75 % of zinc production joins steel in goods. 7 ton Zn associates with 1000 tons of steel. Details of Zn consumption (Fig.1) are as below:



**Fig.1 Share of Zinc consumption**

Prior to discussing the corrosion behaviour of galvanised products, mechanism of corrosion is discussed:

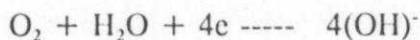
## WHAT IS CORROSION?

Corrosion is the deterioration of a metal because of a reaction with its environment. Also, the corrosion is stated to be an electrochemical phenomenon.

### Criteria for the corrosion to start

- # Anode & Cathode
- # Corrosion potential
- # Metallic path in between anode and cathode
- # Conductive electrolyte

## REACTION



Main culprits  $H^+, O_2, \text{ic-ions}$

## CORROSION COSTS

|   |           |   |                             |
|---|-----------|---|-----------------------------|
| * | UK        | - | L 1300 M/year               |
| * | Australia | - | A\$ 2100 M/year (1.5% GNP)  |
| * | U.S.A     | - | \$ 70 b/year                |
| * | India     | - | Rs 4000 crores              |
| * | World     | - | Rs $2 \times 10^{11}$ /year |

Tonnage of steels are exposed to atmosphere ( marine, industrial, rural and rural cum industrial/marine) in different forms and other. This results in maximum corrosion and contributes to annual cost of corrosion..

## **TYPES OF CORROSION**

- # Uniform corrosion
- # Galvanic corrosion
- # Crevice corrosion
- # Pitting corrosion
- # Intergranular corrosion
- # Stress corrosion
- # De-alloying
- # Erosion corrosion

## **HERE, WE ARE CONCERNED WITH GALVANIC CORROSION**

### **Corrosion Preventive Measures**

- @ **Electrochemical Protection**
  - (i) Anodic protection
  - (ii) Cathodic protection
- @ **Alternation in the medium**
  - (i) Use of inhibitors
  - (ii) Use of scavengers
- @ **Barrier to the environment**
  - (i) Organic coatings
  - (ii) Metallic coatings
  - (iii) Inorganic coatings (non-metallic )
  - (iv) Slushing compounds

## @ Alternation in the metals

- (i) Alloying for higher corrosion resistance
- (ii) Substitution for metal alloys

## @ Proper design of systems

### CATHODIC PROTECTION ( Most effective method)

Cathodic protection is a method to apply a continuous protection current in the reverse direction to the corrosion current. There are two basic methods of applying current , namely

- \* Galvanic current by sacrificial anodes (Zn and its alloys, Al-alloys and Mg-alloys)
- \* Impressed current system by DC rectifier. Methods mentioned are basically to protect immersed/or buried structures. But, we are concerned with sacrificial coating. Here. zinc coating behaves like a sacrificial anode. The Evans diagrams indicate the mechanism of cathodic protection (Fig.2 ).

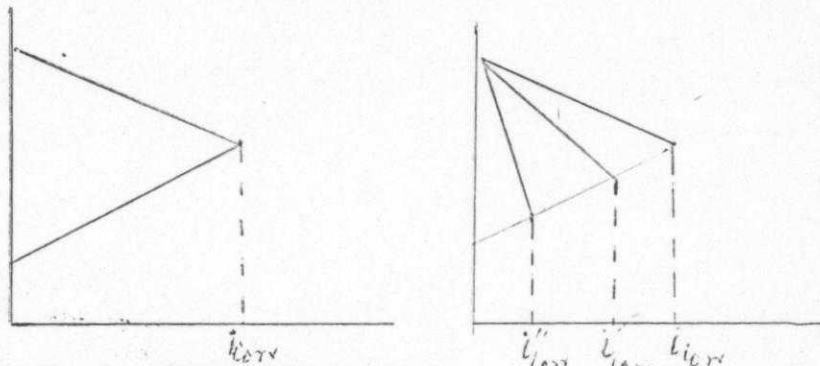


Fig.2 Evans Diagrams

### HOW IT PROTECTS

Zinc dissolves galvanically/or itself when it is in contact with atmosphere containing moisture. It corrodes and liberates electrons as



The electrones so liberated help in protecting the steel cathodically in atmosphere.

### EFFECT OF ALLOYING ELEMENTS ON GALVANISING

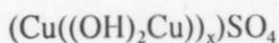
With the aim of increasing the life of structural members in corrosive environments, copper bearing steels popularly known as weathering steels were developed some time back by BISRA in 1913. Buch reported the beneficial effect of copper. The effect was attributed to a combination of copper with sulphur in steel, thus rendering sulphur innocuous Copson found that a protective complex of copper in the rust was formed on weathering steel during

atmospheric exposure. The complex was represented by the formula  $(\text{Cu}((\text{OH})_2\text{Cu}))_x\text{SO}_4$  with maximum of  $x=3$ . A copper complex with  $x=3$  is, therefore, the most protective of the copper sulphate hydroxide.

The work carried out at NML is to found out whether the copper contained in galvanised coating responds similarly in producing the protective copper complex during industrial and marine exposures or not.

The X-ray diffractogram (Fig.3) taken from the outermost layer of the galvanised coating exhibits a peak of Cu, indicating the presence of Cu in the galvanised coating. The EDAX/SEM studies were also carried out on the steel specimens galvanised to obtain the percentage Cu in different inter-metallic layers of the galvanised coating on the steel and also within the weathering steel matrix close to the galvanised coating.

XRD studies were carried out separately on the rust layers formed in marine and industrial environments. These studies revealed the formation of a basic complex of copper in the white rust.



X-ray diffractograms are shown in Fig.4. The copper complex formed in this study corresponds to the maximum value of  $x$  ( $x=3$ ) in the general formula of the complex. The copper complex so formed is believed to fill in the pores of the rust giving a more compact and hence a more corrosion resistant rust layer on galvanized steels.

#### **ALUMINIUM -ZINC ALLOY COATING (GALVALUME)**

Zinc as coating provides excellent galvanic protection to steels, thus preventing rusting of the steel base until the coating itself has been consumed by corrosion. It also provides protection to cut edges. On other hand aluminum coating is more durable than zinc in moist atmosphere. However, aluminium coatings do not galvanically protect steel in rural and industrial environments and rust spots appear at cut-edges. In view of the above, an aluminium -zinc alloy coating (55%+45%) was developed by Bethlehem Steel in 1960. The Al-Zn alloy coating combines the best properties of both viz. greater heat reflectivity of aluminised coatings and better corrosion resistance and better cut edges protection of galvanized coatings.

Fig. 5 indicates that the thickness of Al-Zn alloy coating is greatly influenced by silicon in the coating. At 1.896, the coating thickness gets stabilized. The thickness of coating also depends on the bath temperature. At  $660^\circ\text{C}$ , the coating thickness of 40  $\mu\text{m}$  can be obtained uniformly (Fig. 6).

Table-1 presents the weight loss data of the coatings which were collected by dipping 2"x1" specimens in .5 % NaCl solution at room temperature. The weight loss of aluminium, zinc and Al-Zn alloy coating on mild steel were 0.0786, 0.558 and 0.0938 g/dm<sup>2</sup> respectively at 720 hrs exposure in 3.5 % NaCl solution the data indicate that the dissolution rate of Al-Zn alloy coating was in between the weight losses of aluminium and zinc coatings Addition of zinc (43.2%) in aluminium drastically changed the weight loss without sacrificing the protective properties of Al-Zn alloy.



**Table-1**      **Weight losses of different coatings in 3.5 % NaCl solution at room temperature**

| Time, hrs | Wt loss of Al-coating on steel (g/dm <sup>2</sup> ) | Wt loss of Zinc coating on steel (g/dm <sup>2</sup> ) | Wt loss of Al-Zn alloy coating on steel (g/dm <sup>2</sup> ) |
|-----------|---|---|--|
| 65        | 0.0142  | 0.051   | 0.0162   |
| 163       | 0.0181  | 0.111   | 0.0192   |
| 263       | 0.0258  | 0.132   | 0.0350   |
| 432       | 0.0362  | 0.288   | 0.0671   |
| 648       | 0.0677  | 0.289   | 0.0671   |
| 6688      | 0.0677  | 0.489   | 0.0854   |
| 720       | 0.0786  | 0.558   | 0.0938   |

The effect of NaCl concentration on the potential of different coatings was studied. It appears from Fig.7 that the potentials of both zinc coated and Al-Zn alloy coated steel were above the protective potential and shifted towards more negative values even at 0.5 % NaCl. On the other hand, aluminium coated steel did not attain even the protective potential upto 3 % NaCl. Above 3.5 % NaCl aluminium attained the protective potential (-760 mV vs SCE). This indicates that both zinc and Al-Zinc alloy coatings being very active at all concentrations of NaCl protected the steel efficiently..

Fig. 8-10 show that aluminized coated steel developed rust within 286 hrs in 3.5 % NaCl solution at room temperature, whereas rust on zinc and Al-Zinc alloy coated steels appeared after 720 and 1680 hrs exposure respectively. This shows the superiority of Al-Zn alloy coating over aluminium and zinc coatings.

The effect of the salt spray on the life of Al-Zn alloy coatings was studied for 840 hrs at room temperature and details of it is set-forth in Table-2. It appears from the table that no rust stain was developed on the coating under the conditions mentioned. The loss of the Al-Zn alloy coating was 0.05g/dm<sup>2</sup> whereas the losses of zinc coating, aluminium coating and control 1.3,0.035 and 1.64 g /dm<sup>2</sup> respectively

Typical polarisation curves for Al-Zn coating, galvanised steel and Al-coating in 3.5 % NaCl solution at 30°C are shown in Fig.11. The curves show the superiority of Al-Zn alloy coating over other coatings. Fig. 12 shows the micro-structure of Al-Zn alloy coating on steel..

**Table-2** Salt spray test on aluminium-zinc alloy coated panels; 3.5 % NaCl solution at room temperature.

| Days | Wt loss,g/dm <sup>2</sup> | observation          |
|------|---------------------------|----------------------|
| 5    | -                         | White rust products  |
| 15   | -                         | -do-                 |
| 35   | 0.05 Al-Zn coating        | -do-                 |
|      | 1.30 Zn coating           | -do-                 |
|      | 0.035 Al coating          | -do-                 |
|      | 1.64 (Control)            | Rust stain developed |

Al-Zn coating required two and half times less the thickness of aluminium coating. Less zin coating (20 um) was required for the same corrosion performance (Table-3 )

**Table3** Coating thickness and weight of different coatings

| Coated panels       | Average thickness microns | Coating weight, (Avg),g/dm <sup>@</sup> . |
|---------------------|---------------------------|---|
| Aluminium coating   | 100                       | 5.0                                       |
| Zing coating        | 20                        | 3.2                                       |
| Al-Zn alloy coating | 40                        | 3.7                                       |

Improved bend test performance of the Al-Zn alloy coating may be the result of the following factors:

- \* a thinner intermetallic alloy layer
- \* a softer and less brittle intermetallic layer and
- \* a more ductile Al-Zn alloy layer

At 43.29 % zinc, the Al-Zn alloy coating had a corroded dendritic mircro-structure .

Figs 13-16 show the effect of composition on coating life. In rural, moderate marine industrial atmosphere, the coating fails after 30 years, whereas in severe marine atmosphere, the coating lasts for 15 years. Zinc coating failed within 4 to 5 years. Cumulative world wide production of steel sheet coated with Al-Zn alloy is shown in Fig. 17.

### ZINC-ALUMINIUM (5%) (GALFAN)

The Galfan coating developed by Inland Steel Co, USA contains about 5 % Al which corresponds to the eutectic in the zinc-aluminium system .(Fig.18,19). It, in a humid atmosphere containing SO<sub>2</sub> protect the steel much more effectively. After 20 test cycle, the zinc layer is almost entirely removed (100% corrosion), while coating of zinc alloys is only 18 % corroded. This is due to the fact that the resistance of the alloy is increased by the passivating effect of aluminium, which, furthermore ,inhibits sulphuric acid corrosion.

Compaative polarisation investigation (Fig.20) showed that zinc coating have no passive region,and their dissolution occurs at a particular speed. At the same time coatings of zinc alloys with an aluminium content of over 5 % form a region of passivation in which the corrosion process is retarded sharply.

Above 60°C, the corroion resistance of zinc is reduced sharply and on account of inprovement of the zinc potential in the zinc-steel system,polarity reversal occurs and the protective effect of the coating disappears after 120 hrs,while that of a coating with 5 % Al is retained for 250 hrs. The corrosion resistance of a coating with 5 % Al is higher than that of a normal zinc coating



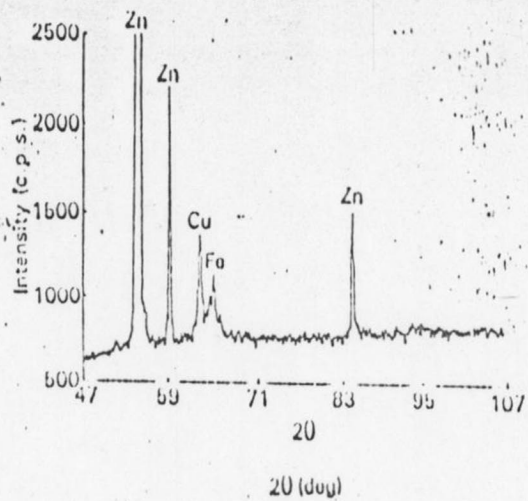


Fig. 3 X-ray diffractogram taken from the outer most layer of the galvanized coating

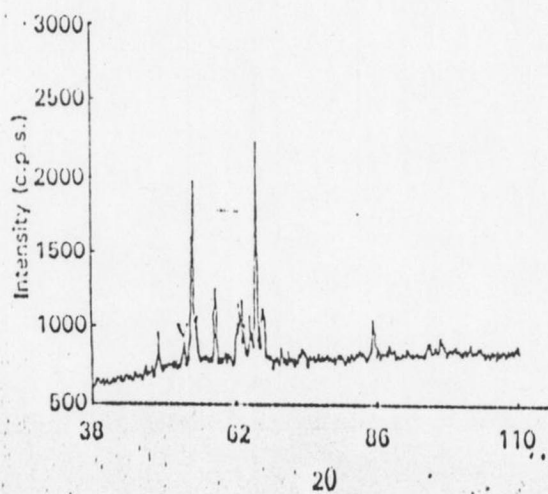


Fig.4 X-ray diffractogram taken from corroded surface of the galvanized steel  
The ( V ) peak corresponds to  $(\text{Cu}((\text{OH})_2\text{Cu}_3))\text{SO}_4$

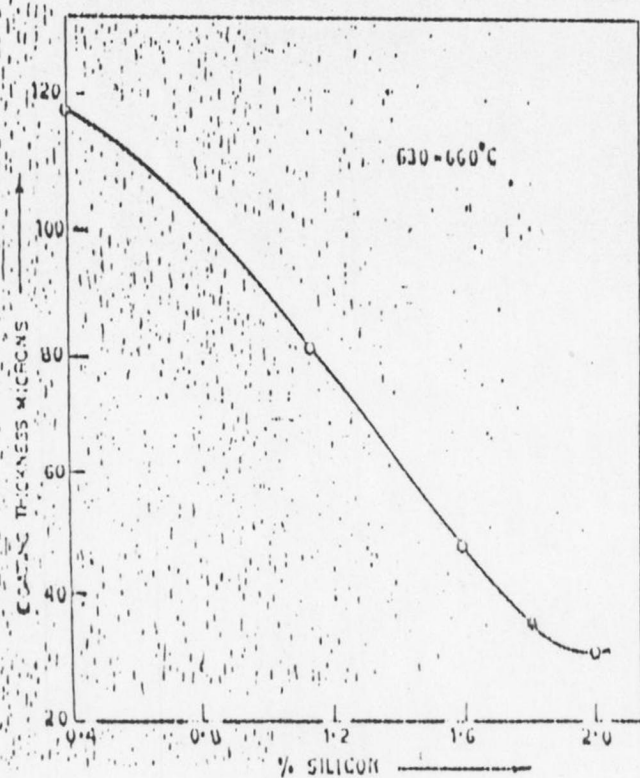


Fig.5 Effect of silicon addition on Al-Zn coating thickness

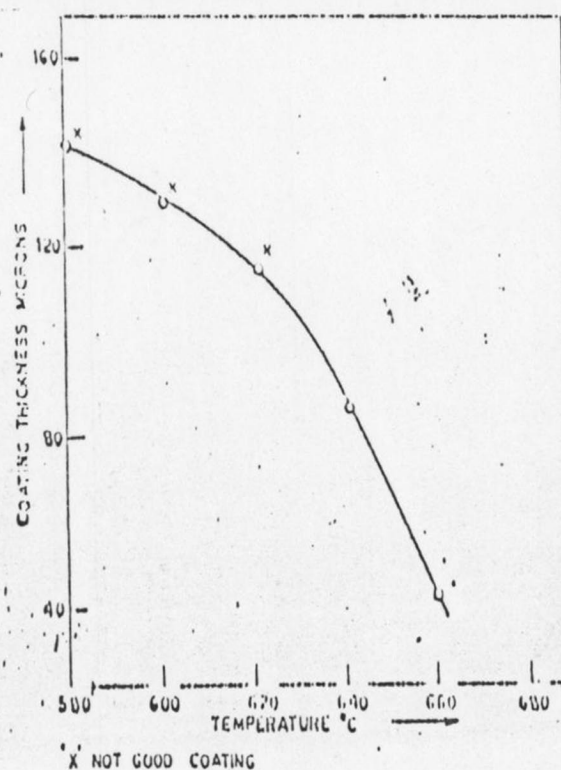


Fig.6 Effect of temperature on Al-Zn alloy coating thickness

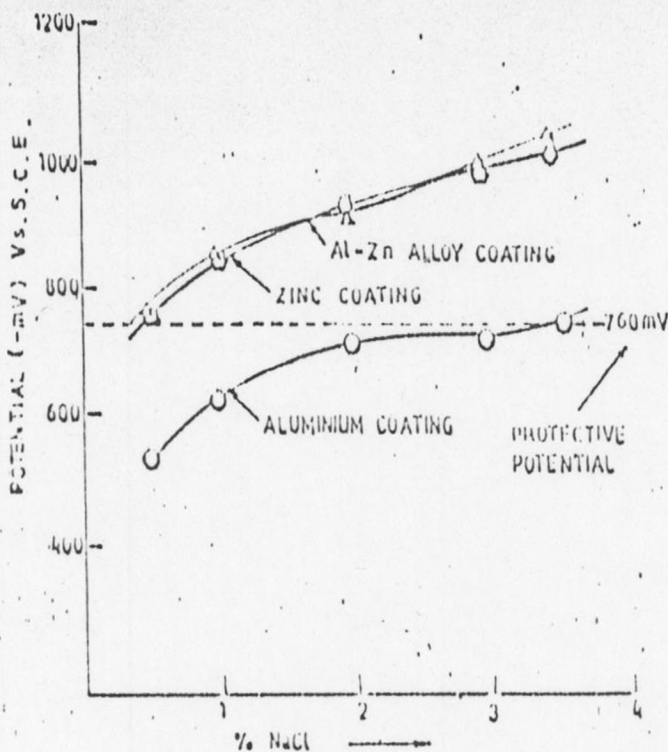


Fig.7 Effect of NaCl concentration on potential

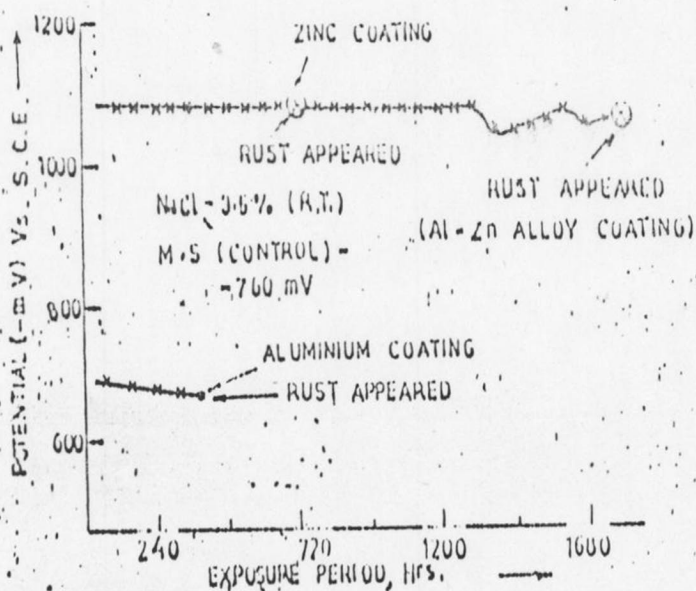


Fig.8 Effect of exposure period on potential

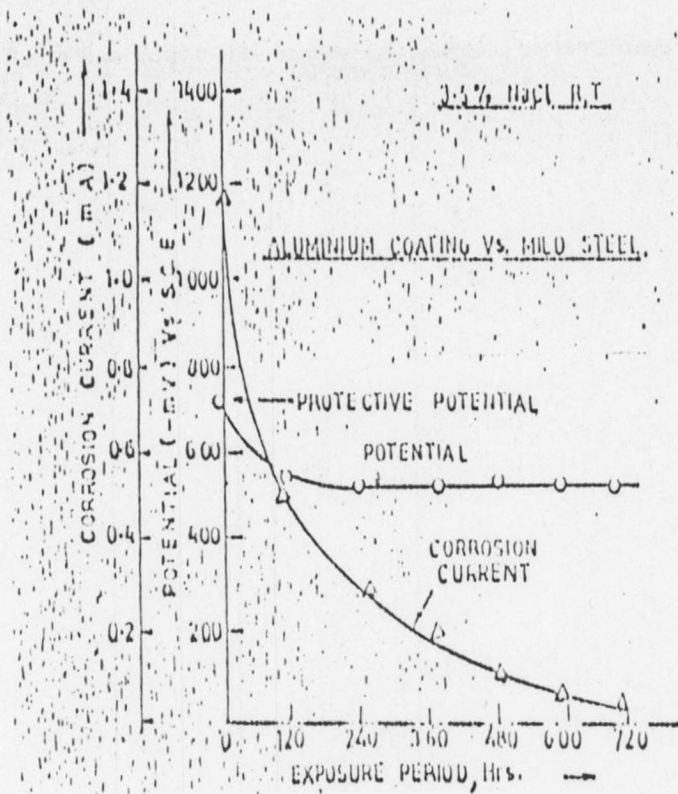


Fig.9 Performance of Al-coating on mild steel in 3.5% NaCl solution

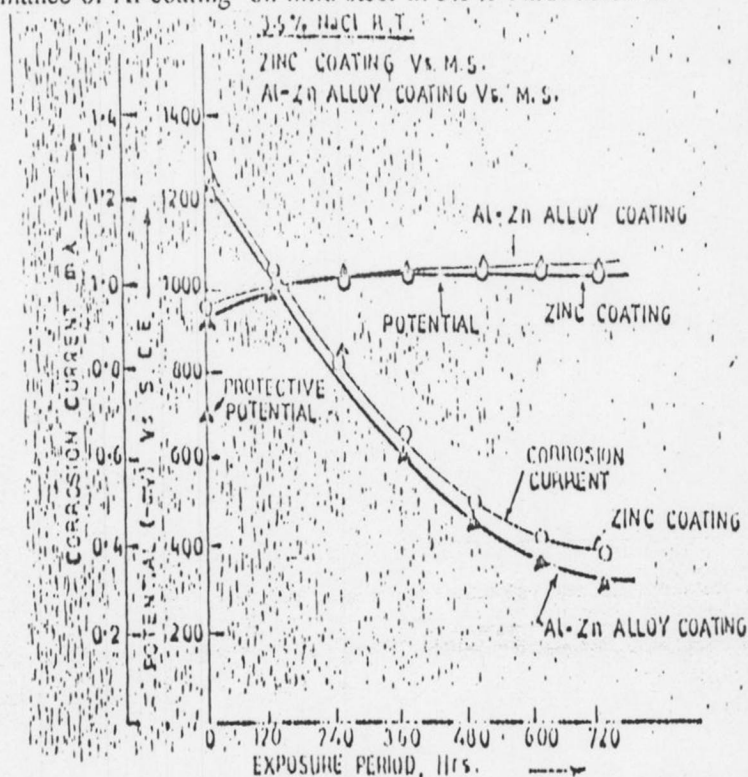


Fig.10

Performance of Zn coating and Al-Zn alloy coating on mild steel in 3.5 % NaCl solution



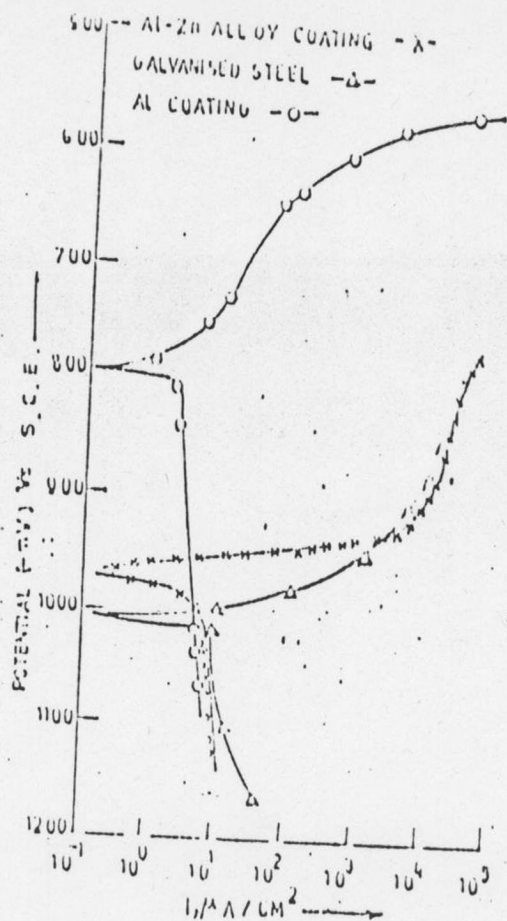


Fig.11 Typical polarisation curves of Al-Zn alloy coating, galvanised steel and Al coating in 3.5 % NaCl solution at 30°C

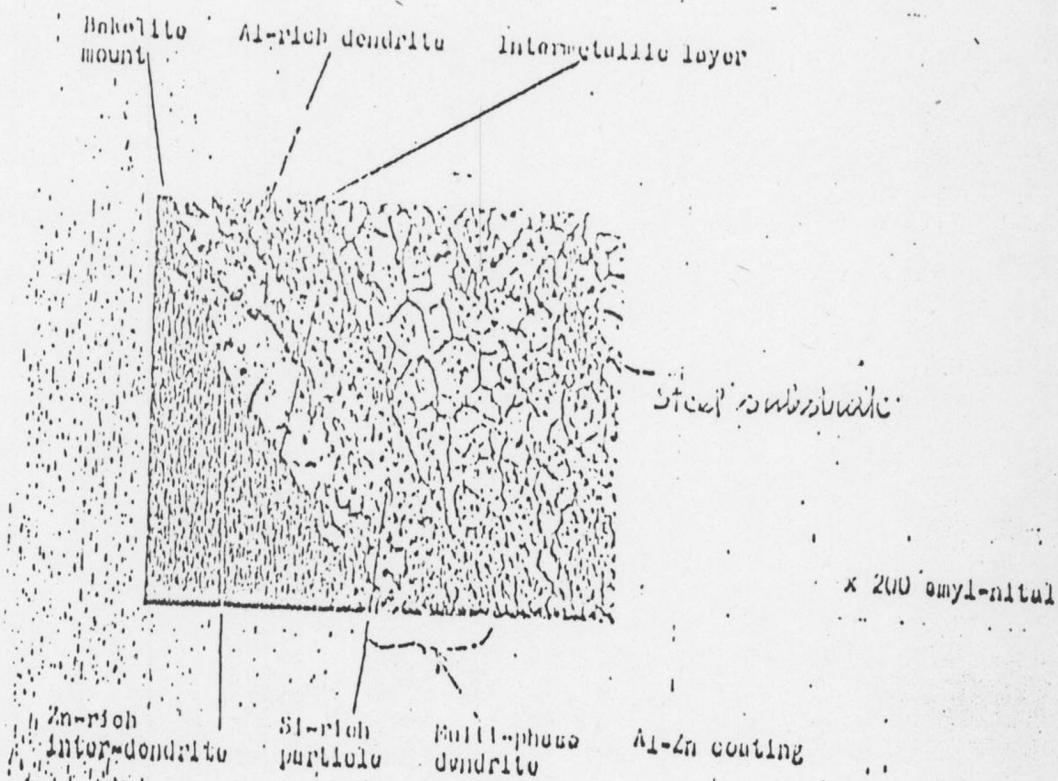


Fig.12

Micro-structure of Al-Zn alloy coating on steel

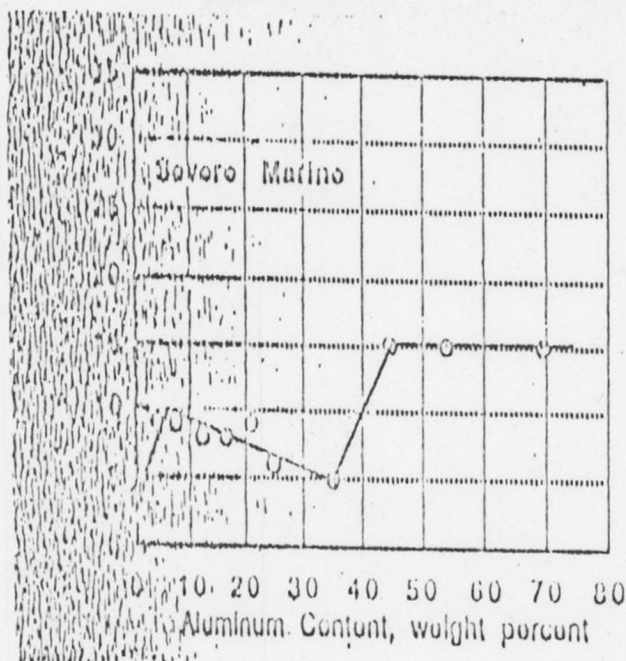


Fig.13

Effect of Al-content on coating life in a severe marine environment

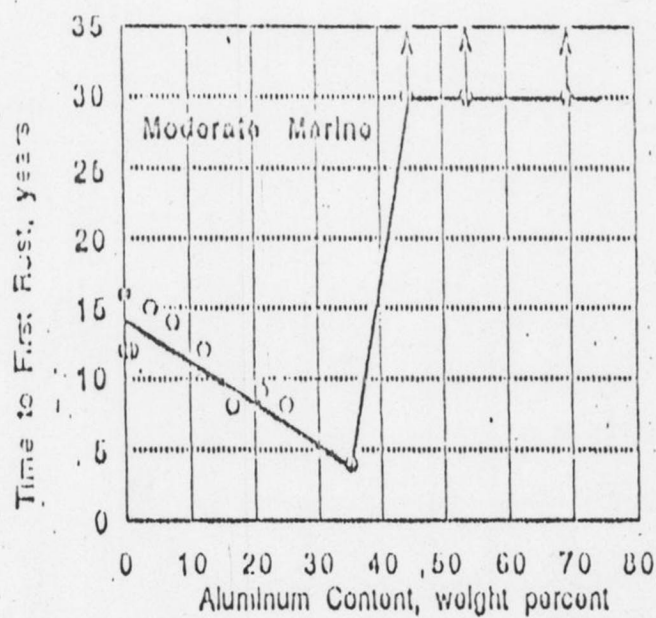


Fig.14

Effect of Al-content on coating life in a moderate marine environment

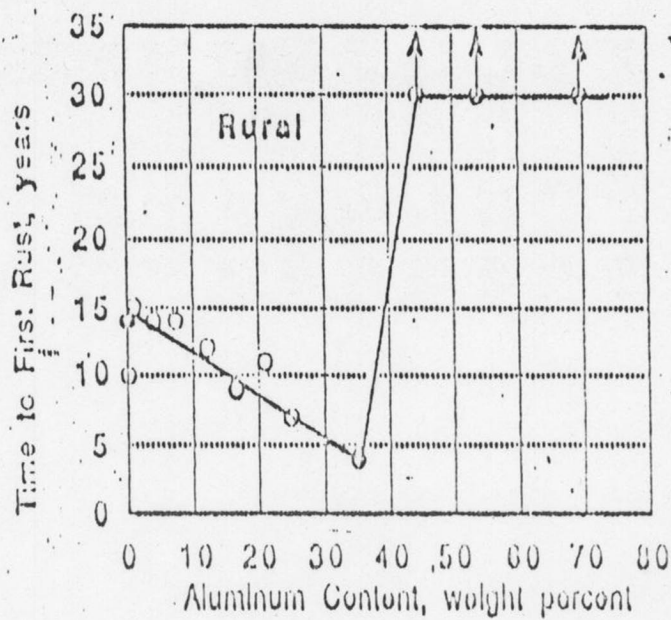


Fig. 15 Effect of Al-content on coating life in a rural environment

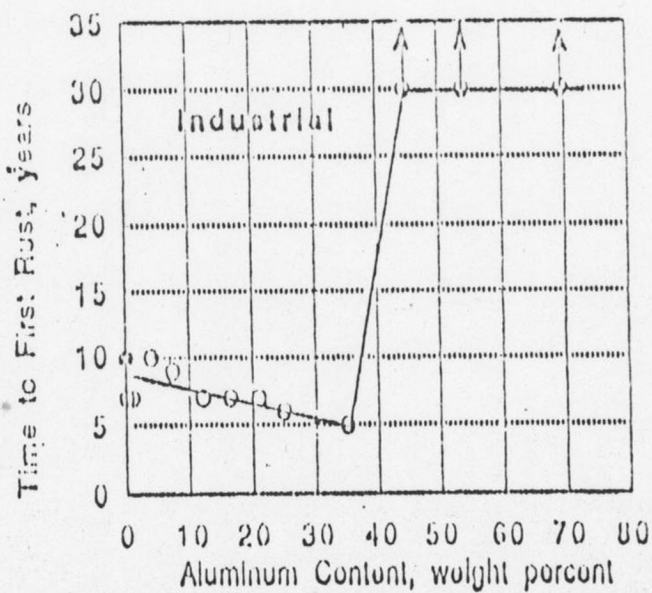


Fig. 16 Effect of Al-content on coating life in an industrial environment

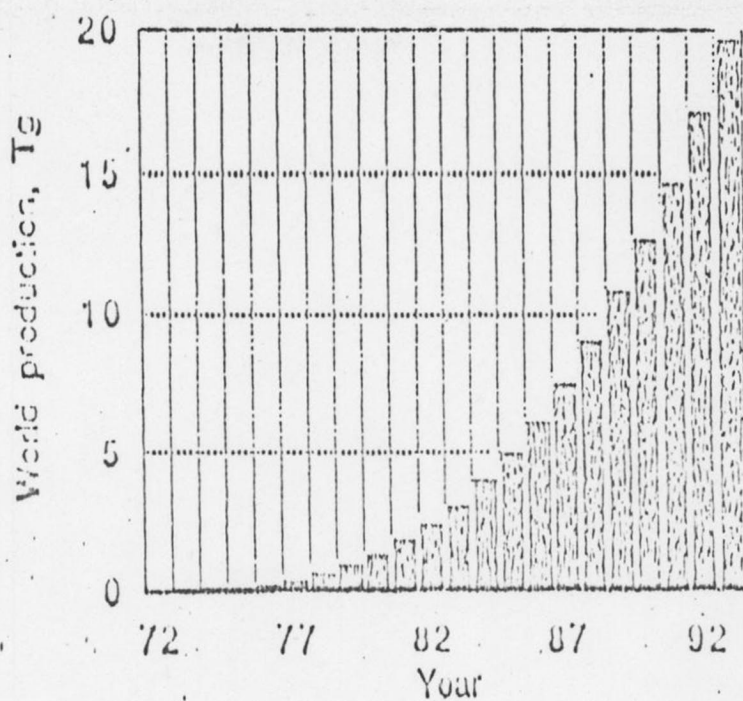
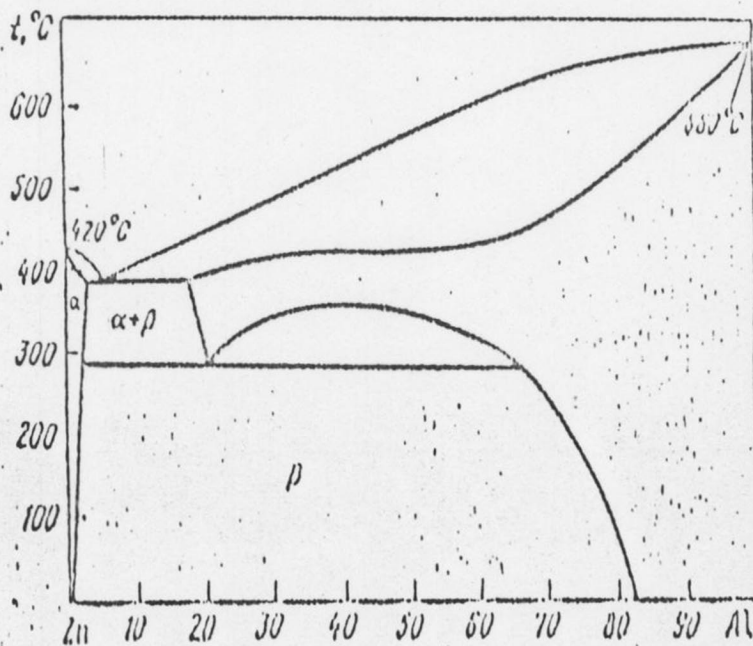


Fig.17

Cumulative world wide production of steel sheet coated with 55 % Al-Zn-alloy (one Tg is equal to 1 million metric tons or 1.1 million short tons )



$\alpha$  Zn base solid solution;  $\beta$  Al base solid solution

Fig.18

Zinc-aluminium phase diagram



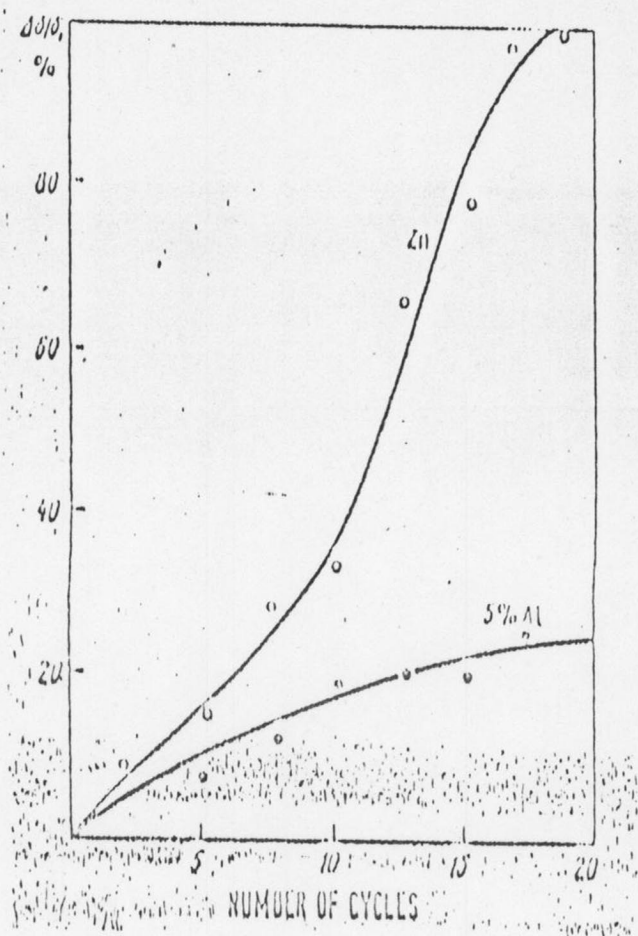


Fig.19 Change in thickness of coating with 5 % aluminium in atmosphere with  $\text{SO}_2$

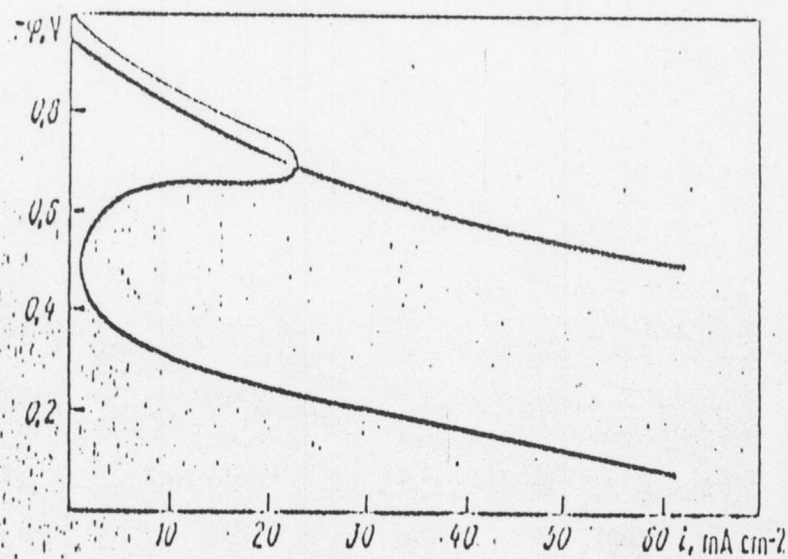


Fig.20 Anode polarisation curves in 3% NaCl solution